

Ground state and excitation properties of the quantum kagomé system $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ investigated by local probes.

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We characterize the ground state and excitation spectrum of the $S = 1/2$, analytically pure and perfect kagomé system $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ using the following measurements: magnetization, muon spin rotation frequency shift K , transverse relaxation time T_2^* , and Cl nuclear spin-lattice relaxation T_1 . We found no sign of singlet formation, no long range order or spin freezing, and no sign of spin-Peierls transition even at temperatures as low as 60 mK. The density of states has an $E^{1/4}$ energy dependence with a negligible gap to excitation.

The study of spin $1/2$ quantum magnetism on the kagomé lattice is very intriguing and lively because different investigation strategies have led to fundamentally different predictions regarding the ground state and excitations of this system. Theories based on numerical or approximate diagonalization of the Heisenberg Hamiltonian favors non-magnetic (singlet) ground state [1, 2] with full symmetry of the Hamiltonian [3], negligible correlation length [4], and an upper limit on excitation gap of $J/20$ [5]. These strategies provide conflicting reports on the possibility of a spin-Peierls state [3, 6]. In contrast, semiclassical treatments based on the thermal [7] or quantum [8] “order from disorder” approach gives rise to a ground state with a broken symmetry of the $\sqrt{3} \times \sqrt{3}$ type, which is stable even against tunneling [10], with gapless magnon excitations [9], and no spin-Peierls type distortion [11]. In these circumstances, one expects experiments to provide some guidance. However, the experimental situation is equally confusing since most of the experimental studies of kagomé-like materials suffered from several kinds of shortcomings, which made comparison with theoretical models difficult. Some material, such as the jarosites [12] have spin $S > 1/2$. Others have $S = 1/2$ but with a non perfect kagomé structure, such as the volborthite $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH}_2)2\text{H}_2\text{O}$ (CVO) [15]. A third class of materials such as $\text{SrCr}_{9p}\text{Ga}_{12-9p}\text{O}_{19}$ [13] and $\text{Ba}_2\text{Sn}_2\text{ZnGa}_{10-7p}\text{Cr}_{7p}\text{O}_{22}$ [14] were hampered by disorder or strong third direction interaction. In light of these difficulties, the recent synthesis [16] of herbertsmithite, $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$, with its Cu-based quantum $S = 1/2$, analytically pure and perfect kagomé lattice, should put the field on a new course.

In this letter we present a comprehensive study of $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ using local probes. In our study, we address four questions which are at the heart of the investigation of the quantum kagomé system: Do $S = 1/2$ spins on kagomé lattice freeze? Is the ground state magnetic? What is the density of excited states, and is there a gap in the spin energy spectra? Finally, does the lat-

tice distort in order to accommodate spin-Peierls state? We address these questions in the present work using nuclear magnetic resonance (NMR) and muon spin resonance (μSR) local probes. We also use magnetization measurements to calibrate the local probes.

$\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ was prepared by hydrothermal methods performed at autogenous pressure. A 800 mL teflon liner was charged with 16.7 g $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (75.5 mmol), 12.2 g of ZnCl_2 (89.5 mmol), and 350 mL water, capped and placed into a custom-built steel hydrothermal bomb under ambient room atmosphere. The tightened bomb was heated at a rate of $1^\circ\text{C}/\text{min}$ to 210°C and the temperature was maintained for 48 h. The oven was cooled to room temperature at a rate of $0.1^\circ\text{C}/\text{min}$. A light blue powder was isolated from the base of the liner by filtration, washed with water, and dried in air to afford 21.0 g product (49.0 mmol, 97.4% yield based on starting $\text{Cu}_2(\text{OH})_2\text{CO}_3$). Magnetic and pXRD data were consistent with those previously reported for herbertsmithite [16].

DC magnetization m measurements were performed on a powdered sample using a Cryogenic SQUID magnetometer at temperatures T ranging from 2 to 280 K and fields H varying from 2 kG to 60 kG. In the inset of Fig. 1 we present mT/H versus T . The data collapse onto a single line, especially at low T , meaning that the susceptibility is field-independent in our range of temperatures and fields. Also, no peak in the susceptibility is observed, indicating the absence of magnetic ordering. The only indication of interactions between spin in these measurements is the fact that mT/H decreases upon cooling whereas in an ideal paramagnetic system this quantity should be constant. Fits of the susceptibility data at high temperatures and lower fields than presented here reveal a Curie-Weiss temperature of $\Theta_{CW} = -314\text{ K}$ [17]. The frustration parameter $T_F/|\Theta_{CW}| \approx 0.22$, where $T_F \sim 70\text{ K}$ is the temperature at which χ^{-1} is no longer a linear function of T , indicates strong geometric frustration. For comparison, in CVO $T_F/|\Theta_{CW}| \approx 1$ [18].

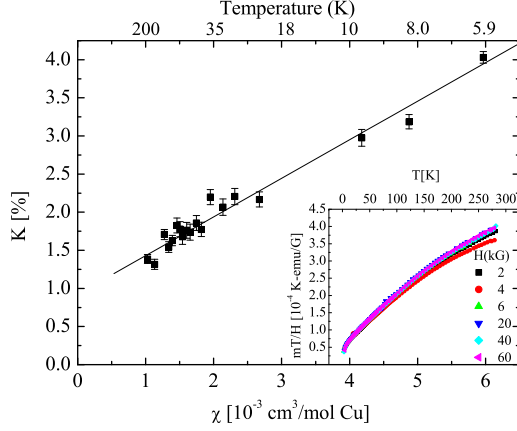


FIG. 1: The muon shift K against susceptibility. In the inset, normalized magnetization versus temperature.

Muon spin rotation and relaxation (μ SR) measurements were performed at the Paul Scherrer Institute, Switzerland (PSI) in the GPS spectrometer with an He cryostat, and in the LTF spectrometer with a dilution refrigerator. The measurements were carried out with the muon spin tilted at 45° relative to the direction of the beam. Positron data were collected in both the forward-backward (longitudinal) and the up-down and right when available (transverse) detectors simultaneously. Data were collected at temperatures ranging from 60 mK to 200 K with a constant field of 2 kG. In GPS we used a resistive magnet with a calibrated field; in LTF we used a superconducting magnet. We took data at overlapping temperatures to calibrate the LTF field. The longitudinal data, which measure muon spin T_1 , were found to be useless since the T_1 in our field range is much longer than the muon lifetime and showed no temperature variations.

In the lower inset of Fig. 2 we show real and imaginary transverse field [TF] data taken at $H = 2$ kG and $T = 100$ K. The data are presented in a rotating reference frame (RRF) at a field of 1.9 kG. The TF asymmetry is best described by $A_{TF} = A_0 \exp(-t^2/(2T_2^{*2})) \cos(\omega t + \phi)$ where T_2^* is the transverse relaxation time, and ω is the frequency of the muon. The quality of the fit is represented by the solid line.

In Fig. 1 we depict the frequency shift, $K = (\omega_0 - \omega)/\omega_0$ where ω_0 is the free muon rotation frequency in the RRF. The difference in frequency between free and implanted muons is a consequence of the sample magnetization; therefore, the shift is expected to be proportional to the susceptibility. Indeed, as shown in the main panel of Fig. 1, there is a linear relation between K and the susceptibility $\chi = m/H$, with the temperature as an implicit parameter; some representative temperatures are shown on the upper axis. In the upper inset of Fig. 2 we present the field dependence of the shift at $T = 10$ K.

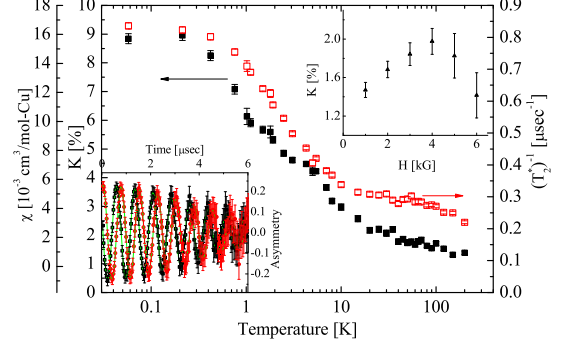


FIG. 2: A plot of the muon shift K , transverse relaxation time σ , versus temperature. In the upper inset, the muon shift K versus external field H . In the lower inset, real and imaginary transverse field asymmetry for $T = 100$ K.

Within the error bars, the shift in the RRF does not depend on the external field. This is in agreement with the susceptibility results. Therefore, Fig. 2 could serve as a conversion graph from muon spin frequency shift to susceptibility.

In the main panel of Fig. 2, we depict K as a function of temperature. An additional axis is presented where K has been converted to χ as discussed above. We find that K (and hence χ) increases with decreasing temperatures and saturates below $T \sim 200$ mK at a value of $\chi = 15.7(5) \times 10^{-3} \text{ cm}^3/\text{mol Cu}$; the error is from the calibration. It should also be pointed out that the energy scale associated with spin $1/2$ in a field of 2 kG is 200 mK, and the saturation could be a consequence of the external field. The saturation of χ is a strong evidence for the lack of impurities in our sample. More importantly, it indicates the lack of singlet formation or spin freezing. The last conclusion is also in agreement with neutron scattering measurements [17] and zero field μ SR [19].

The muon transverse relaxation rate $1/T_2^*$ is also presented in Fig. 2. Roughly speaking, it has the same temperature behavior as the shift (and as the susceptibility). T_2^* relaxation is a result of defects in the sample causing a distribution of muons to electronic spin coupling constants or a distribution of susceptibilities. It has been shown that when the muon relaxation rate behaves similarly to the shift [20] (or susceptibility [21]) upon cooling, it indicates quenched distribution of either the coupling constants or susceptibilities. In this case the relaxation increases simply because the average moment size increases. Since the coupling constants and susceptibility are functions of distances between muon and electronic spin or between two electronic spins, our results are consistent with a lack of lattice deformation in $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$.

Since muons could not reveal dynamic T_1 information,

we performed ^{37}Cl and ^{35}Cl NMR experiments on the same sample. Using the two isotopes, we are able to determine the origin of T_1 . The first step in such a measurement is to find the line shape and to identify the isotopes and transitions. This measurement was done at a constant applied frequency of $\nu_{app} = 28.28$ MHz and a varying external field H . A standard spin-echo pulse sequence, $\pi/2 - \tau - \pi$, was applied, and the echo signal was integrated for each H . In Fig. 3 we show a field sweep for both Cl isotopes obtained at $T = 100$ K. A rich spectrum is found and is emphasized using five x -axis and one y -axis breakers. This rich spectrum is a consequence of the Cl having spin $3/2$ for both isotopes. In the case where the nuclei reside in a site with non cubic local environment and experience an electric field gradient, their spin Hamiltonian could be written as $\mathcal{H} = -h\nu_l \mathbf{I} \cdot (1 + \mathbf{K}) \cdot \hat{\mathbf{H}} + (h\nu_Q)/6 [3I_z^2 - I^2 + \eta(I_x^2 - I_y^2)]$ where ν_Q is the quadrupole frequency, $0 \leq \eta \leq 1$ is the anisotropy parameter, \mathbf{K} is the shift tensor, and $\nu_l = \gamma H/(2\pi)$. The powder spectrum of such nuclei has two satellite peaks corresponding to the $3/2 \longleftrightarrow 1/2$ and $-3/2 \longleftrightarrow -1/2$ transitions, and a central line from the $1/2 \longleftrightarrow -1/2$ transition, which is split due to the powder average. The transition names are presented in the figure. The satellite peaks at $T = 100$ K of ^{35}Cl are at 6.52 and 7.07 T, and for ^{37}Cl at 7.91 and 8.41 T. The lack of singularity in the satellite spectrum indicates that the Cl resides in a site with $\eta > 0$, namely, with no xy symmetry. These findings are consistent with a 3m site symmetry of the Cl ion in the space group $R\bar{3}m$.

In contrast to the two satellites, the splitting of the central lines at $T = 100$ K is clear, and appear for the ^{35}Cl at 6.778 and 6.801 T and for the ^{37}Cl at 8.148 and 8.161 T. Under some assumptions these values could be used to determine the parameter of the nuclear spin Hamiltonian [13]; assuming that the nuclear spin operators, I_x , I_y and I_z are colinear with the principal axes of the shift tensor, and that the in-plane shift is isotropic with $K_{\perp} = (K_x + K_y)/2$, we find for both isotopes, $K_{\perp} \simeq -0.0017(5)$, $K_z \simeq 0.035(9)$ and $\eta = 0.4$, and $^{35}\nu_Q = 3.75$ MHz and $^{37}\nu_Q = 2.55$ MHz. The ratio of ν_Q is as expected from the ratio of the quadrupole moments. Due to the assumptions, the value of K_z should only be considered as an order of magnitude. Nevertheless, it is not very different from that of the muon shift (in the laboratory frame) at the same temperatures. This means that both probes experience a similar field generated by the Cu spins, which for muons is usually a dipolar field.

Temperature dependence field sweeps of the ^{35}Cl central line are shown in Fig. 4. The intensities are in arbitrary units for clarity. The $\pm 1/2 \longleftrightarrow \mp 1/2$ transitions are easily observed at $T = 300$ and 100 K (indicated by the arrows in the figure) but are smeared out at lower T . In fact, the lines become so broad that the NMR shift cannot be followed to low temperature; hence the importance of the μSR results.

Finally, we measured the ^{37}Cl spin-lattice relaxation rate T_1^{-1} to determine spin gap and excitation spec-

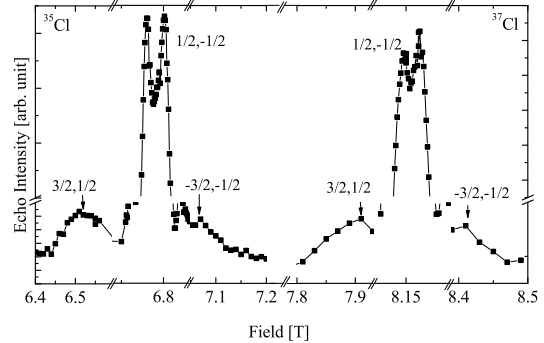


FIG. 3: A field sweep of ^{35}Cl and ^{37}Cl .

trum. The data were taken at a field of 8.15 T which corresponds to the low field peak of the central line. We use a saturation recovery pulse sequence. In Fig. 5 we depict T_1^{-1} normalized by γ^2 where $^{37}\gamma = 3.476$ MHz/T on a semi-log scale. T_1^{-1} increases upon cooling down to 50 K and then sharply decreases. We also present ^{35}Cl $(T_1\gamma^2)^{-1}$ where $^{35}\gamma = 4.172$ MHz/T below 50 K in order to determine the origin of the dynamic fluctuations. These measurements were done under the same conditions as ^{37}Cl . When considering all temperatures we find that $T_1^{35}/T_1^{37} = 0.75(10)$. From a magnetic relaxation mechanism we expect this ratio to equal $(^{37}\gamma/^{35}\gamma)^2 = 0.69$. From a quadrupole based mechanism we anticipate $(^{37}Q/^{35}Q)^2 = 0.62$ where Q is the nuclear quadrupole moment. Our finding is in favor of relaxation mediated by a magnetic mechanism as indicated by the

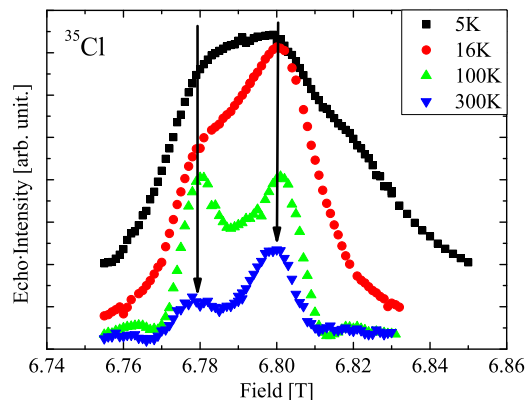


FIG. 4: ^{35}Cl field sweep ($\nu = 28.28$ MHz) at different temperatures. The arrows indicate the central line singularities observed at high- T but smeared out at low T .

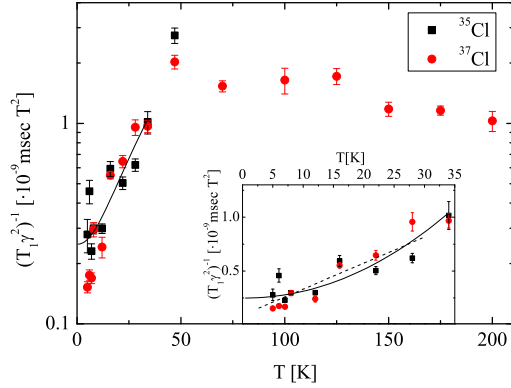


FIG. 5: A semi-log plot of the Cl inverse spin-lattice relaxation, $(\gamma^2 T_1)^{-1}$, versus temperature. Inset, a linear plot of the low-temperature region. The black line is a fit to Eq. 1. The dashed line is straight.

overlapping $(T_1 \gamma^2)^{-1}$ data points in Fig. 5.

In the inset of Fig. 5 we zoom in on the low T data using a linear scale. A first glance suggests that at low temperature $1/T_1$ is a linear function of T as indicated by the dashed line. A remanent relaxation at zero temperature $1/T_1^n$ could be due to magnetic fluctuations from other nuclear moments such as the protons or copper, since they continue to fluctuate even when the electronic moments stop. Thus the spin lattice relaxation due to electronic contribution only $1/T_1^e \equiv 1/T_1(T) - 1/T_1^n$ obeys $1/(T_1^e T) = \text{const.}$ This relation is expected in the case of free fermions and might be related to recent theories [22, 23].

A different approach to T_1 interpretation is in terms of magnon Raman scattering where

$$\frac{1}{T_1}(T) = \frac{1}{T_1^n} + \gamma^2 A^2 \int_{\Delta}^{\infty} \rho^2(E) \cdot n(E) \cdot [n(E) + 1] dE \quad (1)$$

with ρ being the density of states, Δ the gap, A is a constant derived from the hyperfine coupling, and $n(E)$ the Bose-Einstein occupation factor [24]. This expression is constructed from the population of magnons before and after the scattering, with the associated density of states and the assumption that they exchanged negligible amount of energy with the nuclei since its Zeeman splitting is much less than a typical magnon energy. However, in frustrated magnets the magnon might not be the proper description of the excitations [13, 14]. Nevertheless, we use Eq. 1 since it is expected for any kind of bosonic excitations, and since there is no other available theory. We assume $\rho(E) \sim E^\alpha$, with α and Δ as fit parameters. The fit of Eq. 1 to the data is presented as the solid line in Fig. 5, and in its inset. We find $\alpha = 0.23(1)$ and $\Delta = 0.5(2)$ K. Comparing to $J = 209$ K [17], this is a negligibly small gap. It indicates that most likely there is no gap in the spin energy spectra, in agreement with Ref. [17], and $\rho(E) \sim E^{1/4}$.

To conclude, susceptibility measurements down to 60 mK suggest that there is no freezing and only a saturation of susceptibility, namely, no singlet formation. The data also do not support the presence of lattice deformation. Finally, Cl NMR T_1 measurements find a negligibly small magnetic gap and the density of states $\rho \sim E^{1/4}$. Thus, $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ is an exotic magnet with no broken continuous symmetry but gapless excitations. It might be an example of algebraic spin liquid [23].

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